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13. ABSTRACT (Maximum 200 words) An optimal reduced space method for capturing the low-frequency motion in a classical molecular dynamics calculations is presented. This technique provides a systematic means for carrying out reduced-dimensional calculations in an effective set of reduced coordinates. The method prescribes an optimal reduced subspace linear transformation for the low frequency motion. The method is illustrated with a dynamics calculation for a model system, where the original six-dimensional space is reduced to two (three) dimensions, depending on the desired frequency cutoff value.				
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- (a) High Dimensional Model Representations, G. Li, C. Rosenthal, and H. Rabitz, J. Phys., Chem. A, 105, 7765-7777 (2001)
- (b) Optimal reduced dimensional representation of classical molecular dynamics, BK Dey, H. Rabitz and A. Askar, L. Chem Phys., 119, 5379 (2003)
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(4) Research Summary:

Classical molecular dynamics is an important tool in chemistry for many applications, e.g., proteins, energetic materials, etc.^{1,2} Such dynamical studies are computationally time consuming because of the large number of degrees-of-freedom and the coupling amongst them. Experience suggests that all of the degrees of-freedom or all of the frequency components will not be equally important for most dynamical processes. Current simulation times out to a few nanoseconds are much shorter than the time scales of many important conformational processes and this situation poses a major obstacle limiting the usefulness of classical molecular dynamics simulations. Many attempts,³⁻¹⁷ aimed at containing the system dimensions have been made over the years to aid in the effort to extend the time scale of the simulations, but as yet, no fully satisfactory solution has been found.

One approach^{5,6} is principal component analysis (PCA), also known as the Karhunen-Loeve expansion in time series analysis. The method has been employed with the hope of describing molecular dynamics trajectories in terms of a small number of variables or essential degrees of freedom.^{7,9,10,22-24} here one determines a small number of important modes by PCA and projects the equation of motion on the resulting low dimensional vector space. This method has been successful in treating hydrodynamic systems,¹¹ but not as satisfactory in molecular dynamics simulations.²⁵

Another way in which the dimensionality may be reduced is by neglecting some degrees of freedom so that the corresponding motions are not present. Some dynamical processes can be modeled quite well in this way. For example, intramolecular vibrational energy relaxation for the overtones of planar benzene can be well described by a four-atom model.¹² However, such models are often oversimplified. A somewhat higher level

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of sophistication of this same idea has been suggested.¹³⁻¹⁶ and constrained classical dynamics approaches have also been introduced.¹⁷⁻²¹ For example, in an application¹⁹ to the classical motion of a polyatomic system with internal coordinate constraints, the unconstrained positions were calculated first, and then the constraint equations were solved for the undetermined multipliers from which the displacements were obtained. An application of this idea was performed²¹ for the intramolecular dynamics of HONO.

Filters may be used for removing the unwanted frequencies from signals.²⁶⁻²⁸ A proposal along these lines used a filter to remove the high frequency motion from a set of stored atomic coordinates, allowing the important motions within the simulation to be observed more easily.²⁹ The wavelet transform has also been used³⁰ in the analysis of molecular dynamics trajectories. The Fourier transform basis set is localized in frequency but the wavelet basis set is localized in time as well, resulting in resolution of time localized rare events. Besides filtering and constraint-based reduction of dimensionality, another approach consists in altering the potential energy function by adding extra forces³¹ or by a parametric additive potential correction term.³² By properly choosing the additive term, the trajectories can be smoothed by removing unwanted oscillations.

In general, the amplitude associated with any degree of freedom will typically depend on many, possibly all, of the degrees-of-freedom of the system. We seek a representation of the dynamics of a system with N -degree of freedom in terms of a surrogate system with fewer degrees of freedom. Along these lines^{33,34} previous works by the group at Princeton, introduced the notion of subspace dynamics. The subspace was selected from the eigenvectors of the locally linearized system based on a high frequency cutoff of the spectrum. These eigenvectors were used to project the full dynamical equations into the subspace leading to a small number of effective dynamical equations of motion for the system. Recently, a reduced space dynamical method based on orthogonal decomposition of the eigenmodes has been successfully applied to treat fluid dynamics problems.^{35,36}

This research studied the subspace method^{33,34} more systematically based on optimally designing the subspace where the original set of dynamical equations are projected onto another reduced set of effective equations. We used a genetic algorithm to identify the subspace. This is a general approach for reducing the dimensionality of a system, effectively filtering out the unwanted high frequency parts of the collective dynamics and thereby permitting an exploration of the low frequency average properties of the system. The research development aims to present the basic concept of seeking an optimal low dimensional subspace for long time dynamical motion.

This new subspace method seeks an optimal subspace of dimension M from its parent full space of dimension N such that $M < N$ by suitably defining a cost function. A

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search is performed to identify the optimal transformation relating the N - and M -dimensional spaces under the desire to capture the low frequency system motion. The demonstration of the method with a model potential revealed that the dynamics in the subspace acted like a filter for the high frequency motions, automatically determining the essential low frequency motion. The choice of the cutoff frequency plays an important role in this method. It is crucial that the subspace dimension, M be consistent with the frequency cutoff. In its full form the approach can be applied to systematically perform long time scale dynamics. The present research focused on the essential aspects of the algorithm that seeks out a subspace keeping in mind applications to long time scale conformational molecular dynamics. The demonstrations in the research were chosen with simple model systems to test the optimal subspace method. Future applications of the method would be for polyatomic molecules, with significant long time behavior.

The subspace method differs from the constrained molecular dynamics method where some degrees of freedom are eliminated through the introduction of holonomic constraints so that the associated momenta are zero. However, under realistic conditions, no matter how stiff some of these degrees of freedom (bond lengths, bond angles, etc.) may be, the associated momenta are not zero. At thermal equilibrium, there is a Boltzmann distribution of these momenta, and the constrained dynamics can differ significantly from the true behavior. This can result in the constrained dynamical trajectories covering a different region of phase space than the true trajectories. The subspace method, in this regard, does not force any coordinates to be irrelevant and the associated conjugate momenta are not set to zero. Thus, the subspace method is more flexible than the constrained dynamics method. In this regard, the method can automatically identify the important slow structural degrees of freedom. A full algorithm would identify successive subspaces following the dynamics in much the same way done before where the subspace was defined by the local Hessians. The present method is more flexible and further generalization will be presented elsewhere permitting a larger subspace. This would better account for the equilibrium averages associated with the trajectories than the usual constrained dynamics method.

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